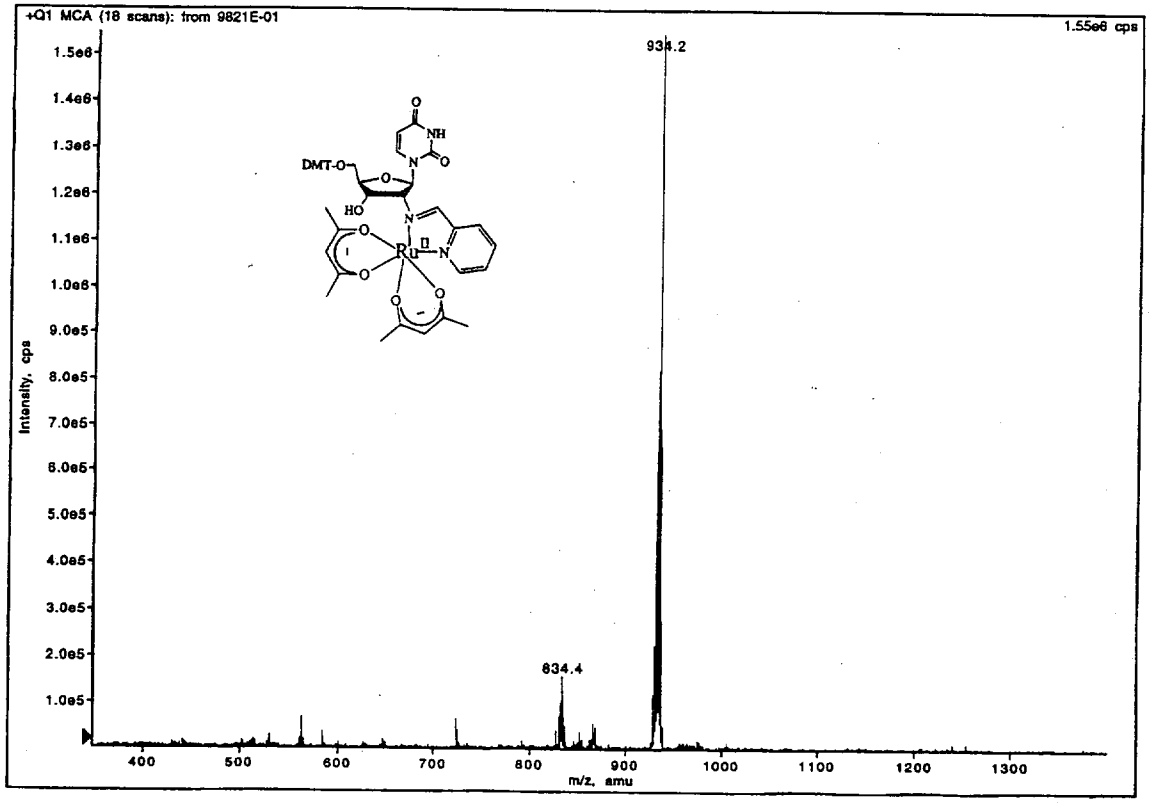
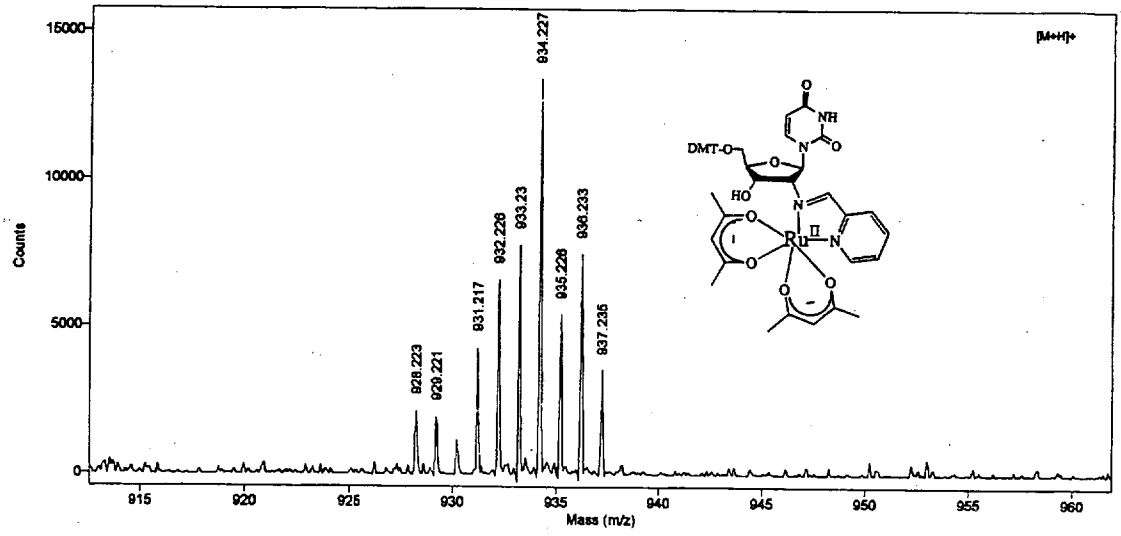
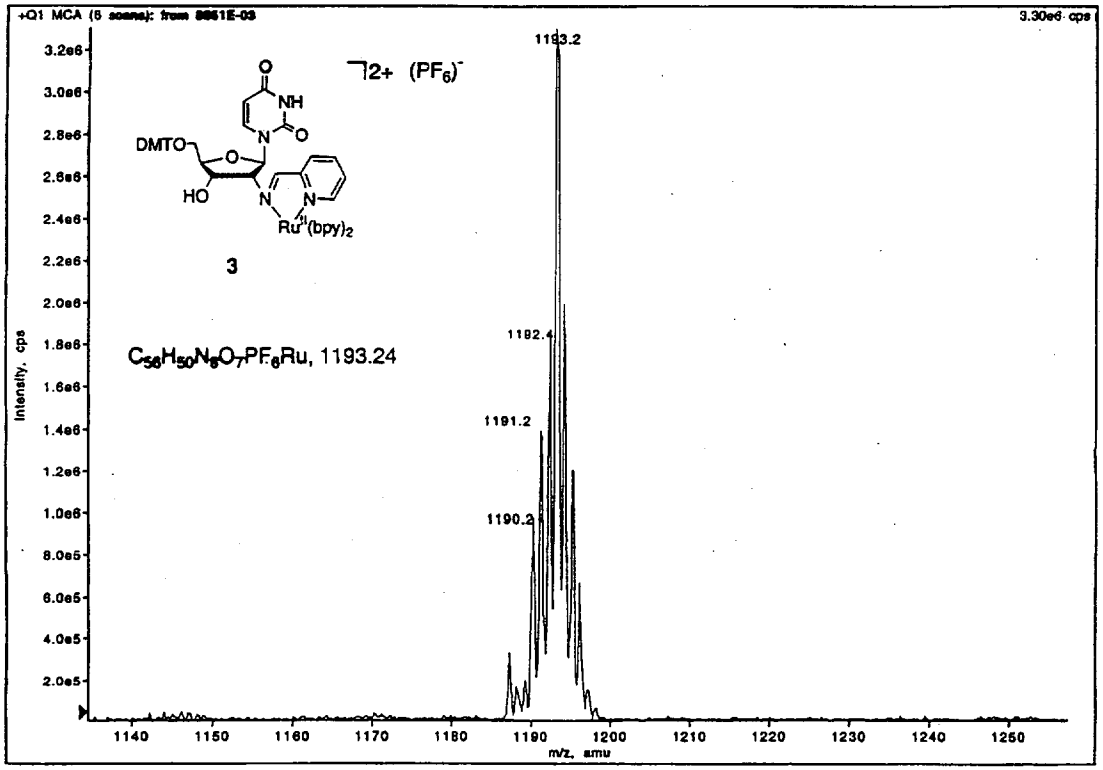
ESI mass spectrum of **2** (positive ionization mode).

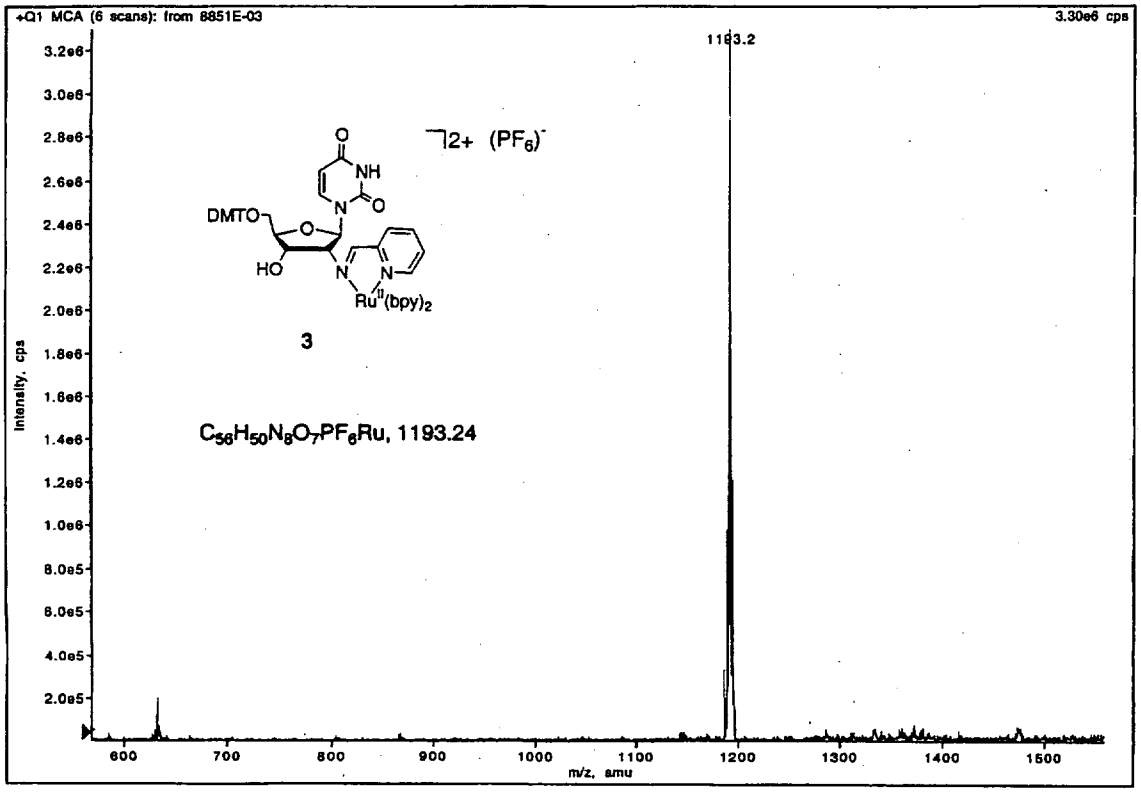


MALDI-TOF spectrum of **2** showing isotopic distribution (positive ionization mode).

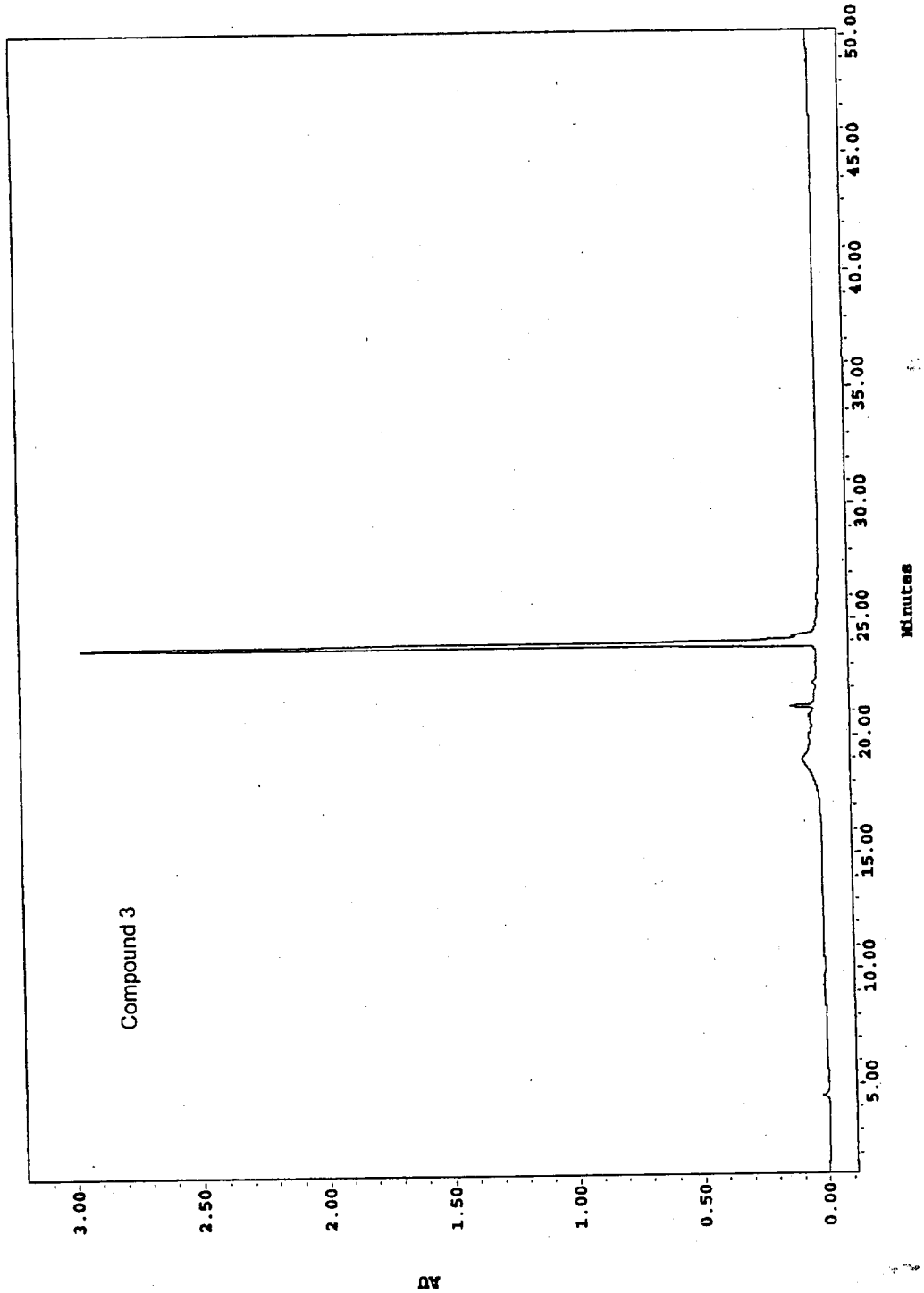


ESI mass spectrum of **3** (positive ionization mode).

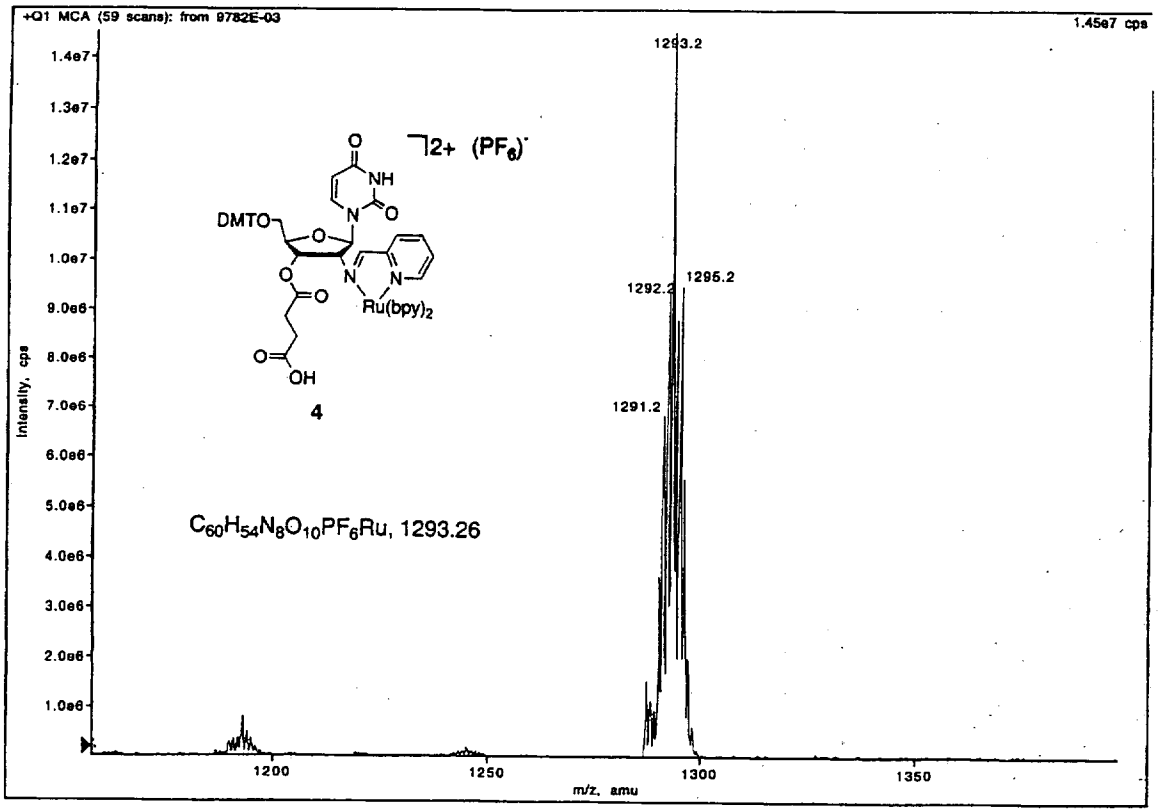


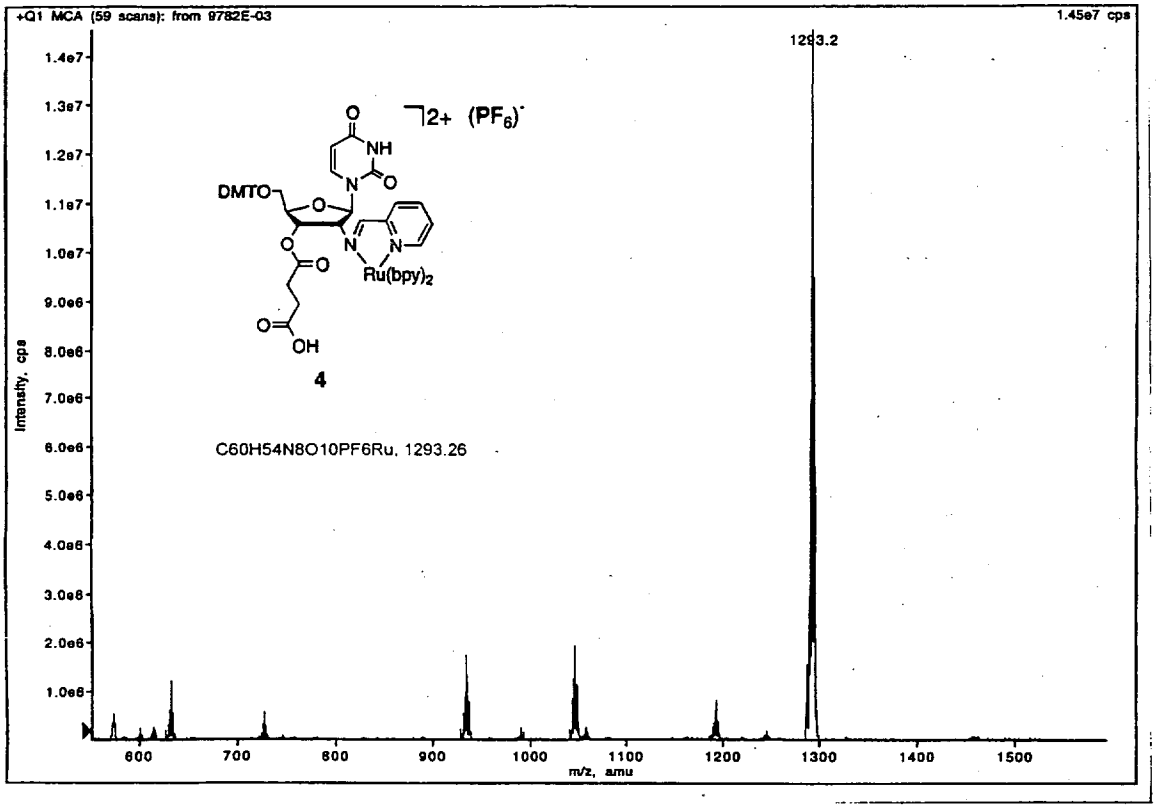


Analytical HPLC trace of **3**. (Column: Prism C18. Gradient: 0-40% B over 15 minutes. Solvent A = 0.1 M triethylamine acetate, pH 7.0, 2% acetonitrile; Solvent B = acetonitrile).

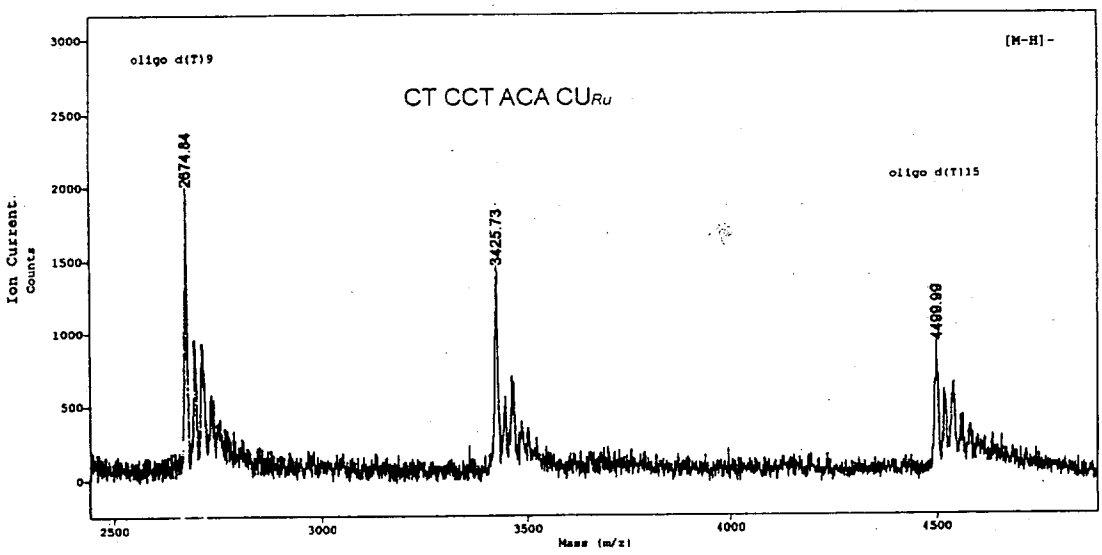


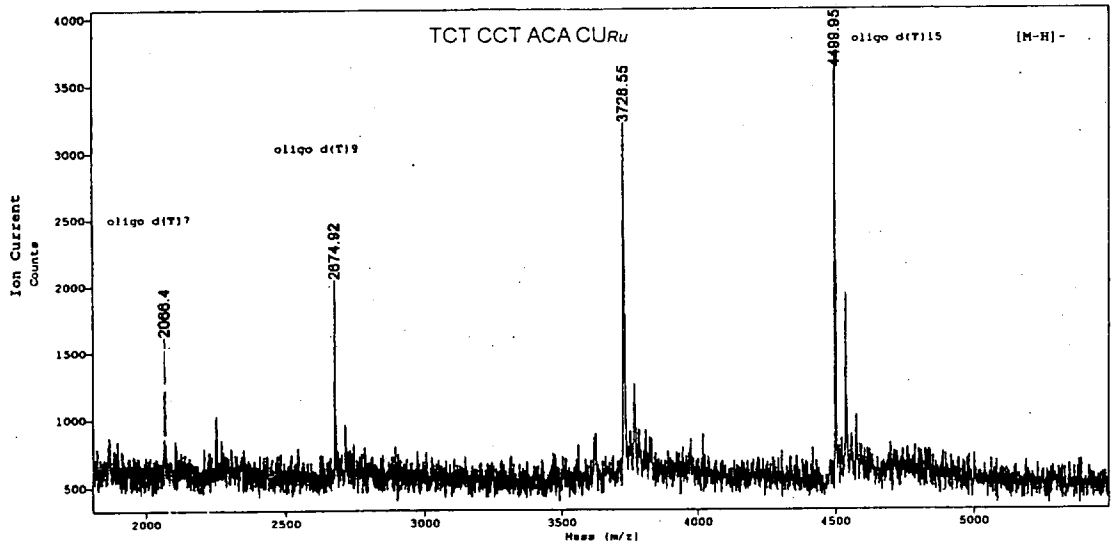
ESI mass spectrum of **4** (positive ionization mode).



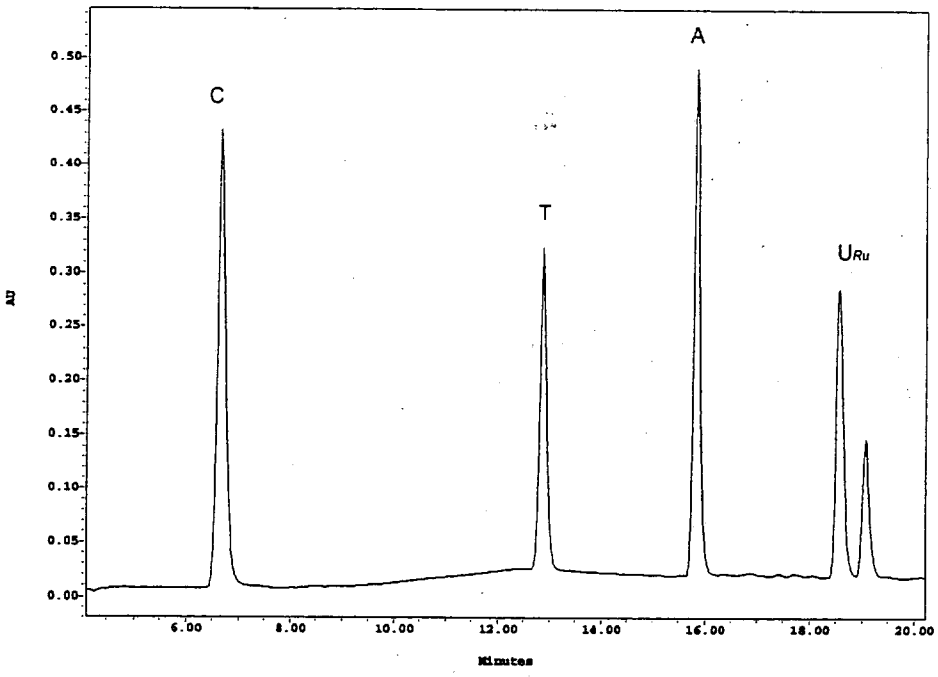


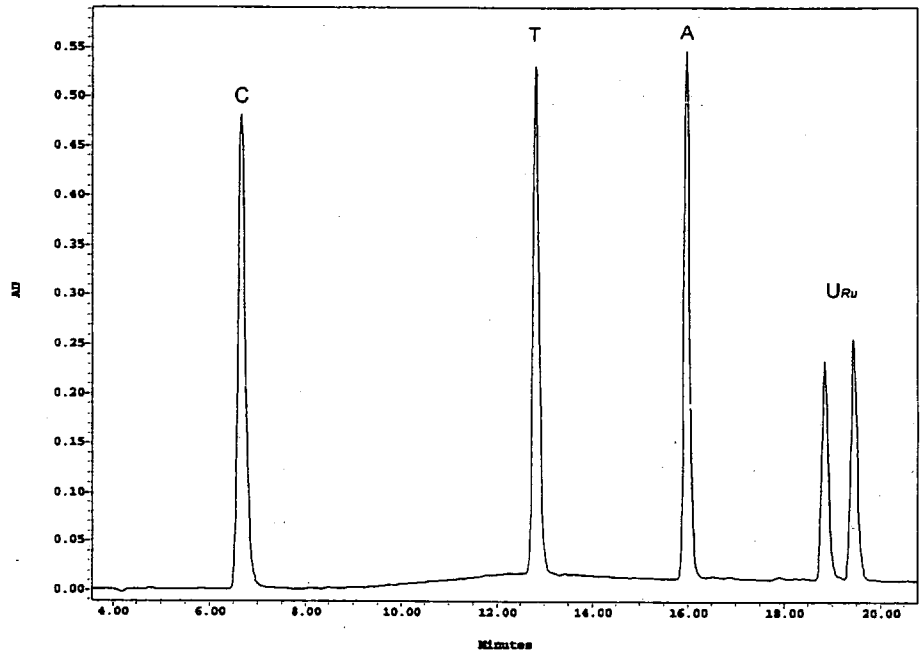
MALDI-TOF mass spectra for ruthenium-containing oligonucleotides, **6** (top) and **7** (bottom). Calculated for **6**: 3425.56 [M-H]$^-$. Calculated for **7**: 3730.76 [M-H]$^-$. Peaks corresponding to internal standards are noted.



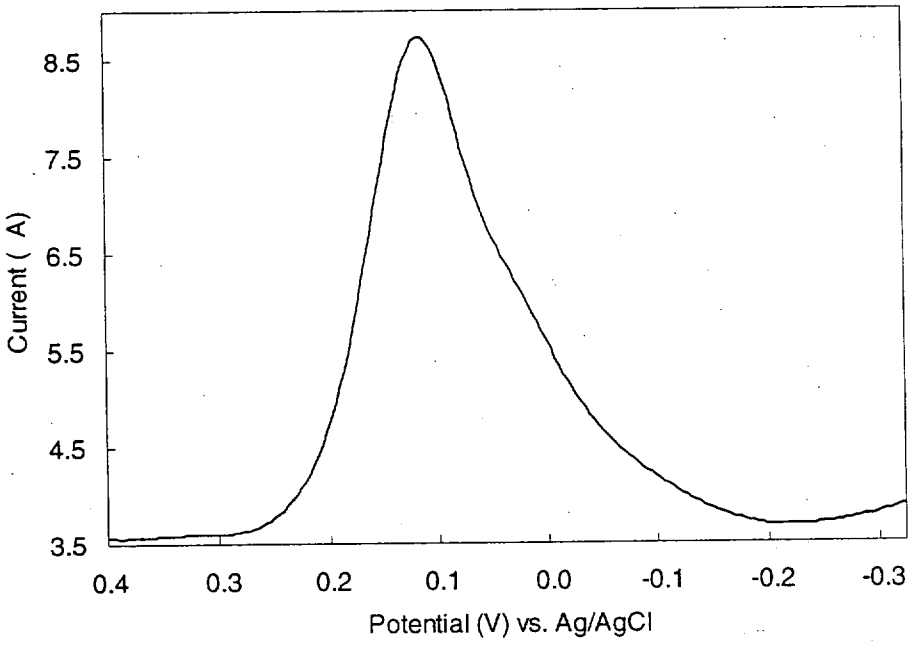


Products of enzymatic digestion of **6** (5′-CTCCTACACU$_{Ru}$) (top) and **7** (5′-TCTCCTACACU$_{Ru}$) (bottom) as analyzed by reverse-phase HPLC. Integration of the peak areas gives 5C:2T:2A:1U$_{Ru}$ for **6** and 5C:3T:2A:1U$_{Ru}$ for **7** (λ = 260 nm). (Column: Prism C18. Gradient: 0-17% B over 15 minutes, then 17-75% B over 15 minutes. Solvent A = 0.1 M triethylamine acetate, pH 7.0, 2% acetonitrile; Solvent B = acetonitrile). See Experimental Section for peak assignments.

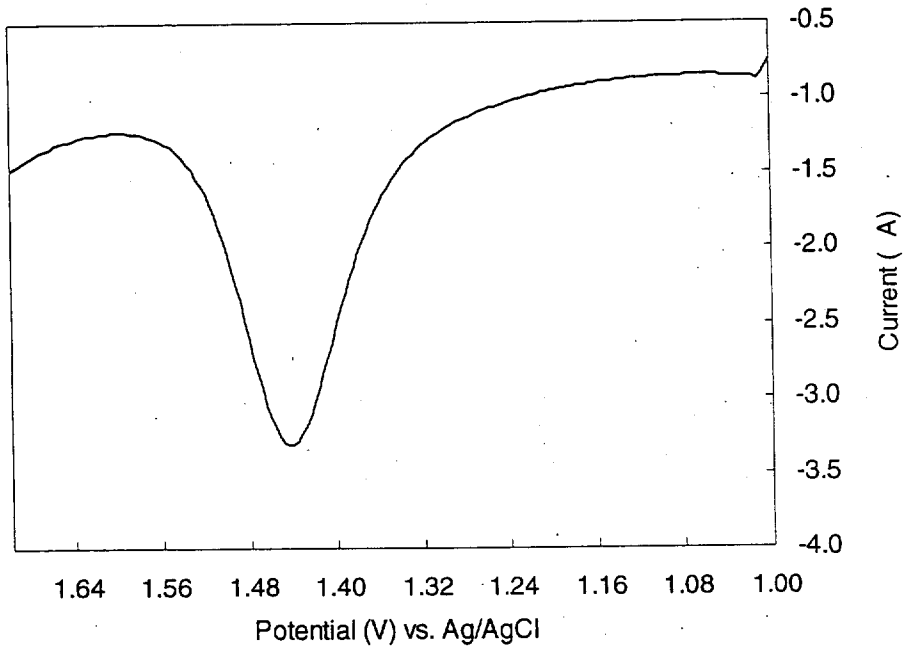




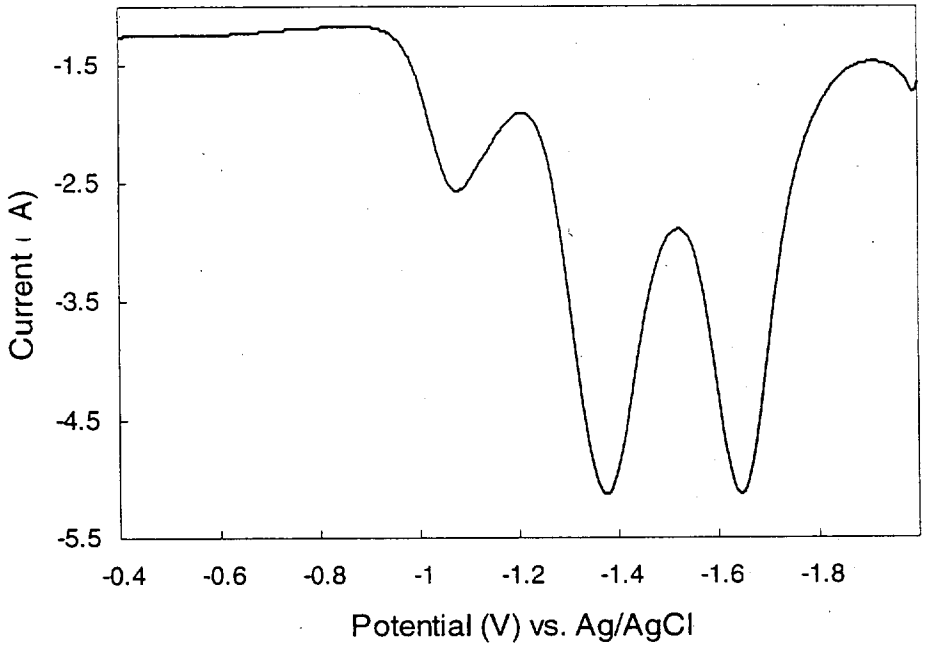
A sample differential pulse voltammogram of **2** recorded in ethanol containing 0.1 M $NH_4^+PF_6^-$ (initial potential = 0.4 V; final potential = -0.4 V; frequency = 15 Hz).



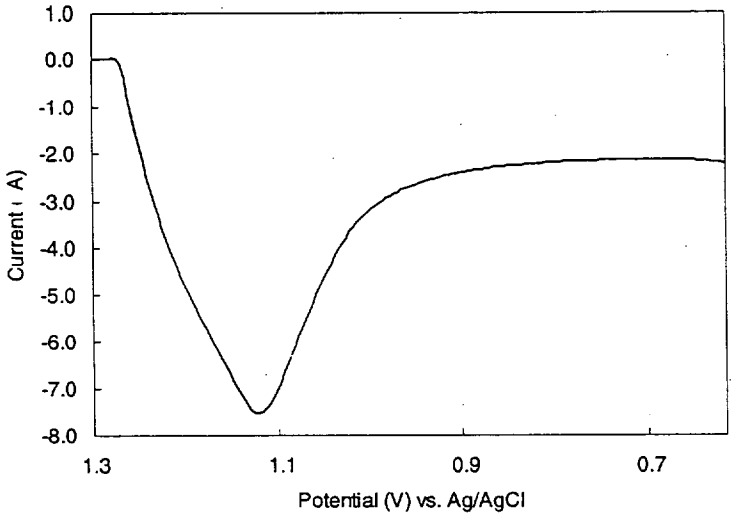
A sample square-wave voltammogram of **3** recorded in dichloromethane containing 0.1 M TBAH (initial potential = 1.0 V; final potential = 1.7 V; frequency = 15 Hz).



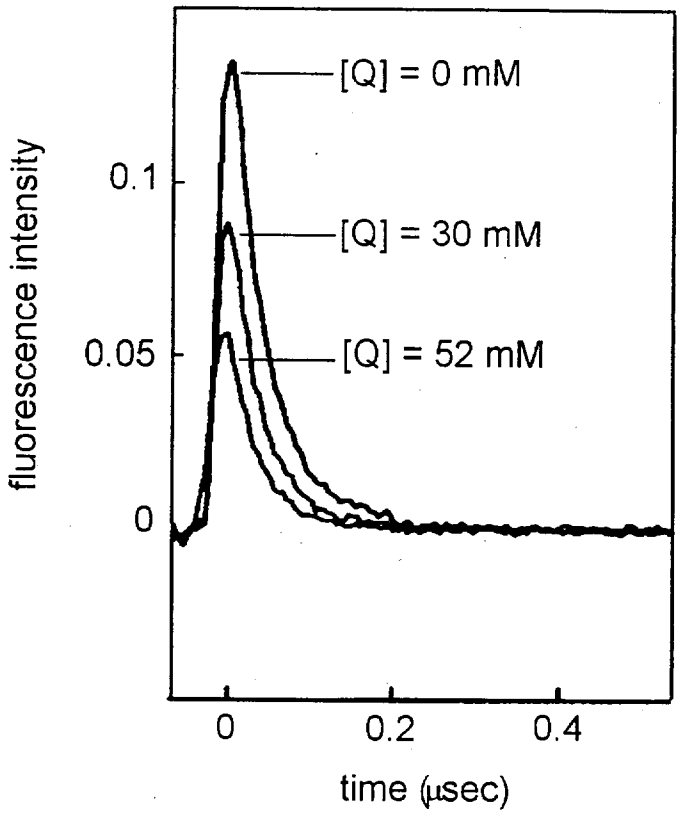
Differential pulse voltammogram showing ligand centered reductions of **3** in acetonitrile containing 0.1 M TBAH.



A sample square-wave voltammogram of oligonucleotide **7** in 50 mM sodium phosphate (pH 7.0) containing 500 mM sodium chloride.



Plot of excited-state lifetime of duplex **7:9** (35 μM) in the presence of $[Ru(NH_3)_6]^{3+}$ (0, 30, and 52 mM). Buffer: 50 mM sodium phosphate (pH 7.0), 500 mM sodium chloride. Excitation wavelength = 480 nm; observation wavelength = 720 nm.



A sample Stern-Volmer plot derived from quenching experiments involved photoexcited **7:9** (35 micromolar) in the presence of $[Ru(NH_3)_6]^{3+}$ (12-52 micromolar). Inset = transient absorption trace at 450 nm. (Buffer = 50 mM sodium phosphate (pH 7.0), 500 mM sodium chloride).